



Effect of Fe on the photocatalytic removal of NO_x over visible light responsive Fe/TiO₂ catalysts



Jinzhu Ma, Hong He*, Fudong Liu¹

State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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ABSTRACT

We synthesized different Fe/TiO₂ catalysts and studied the influence of Fe on the structure and performance of Fe/TiO₂ as a photocatalyst to remove gaseous NO in air under visible light. The electron paramagnetic resonance results revealed that Fe ions substituted the Ti ions of TiO₂ prepared by co-precipitation and homogeneous precipitation method. More Fe ions were incorporated into the crystal lattice of TiO₂ prepared by co-precipitation method than that prepared by homogeneous precipitation method. No Fe ions were incorporated into the crystal lattice of TiO₂ prepared by conventional wet impregnation method. Furthermore, Fe doping influenced the UV–vis absorption and photoluminescence of TiO₂. The higher photocatalytic activity of Fe/TiO₂ prepared by co-precipitation method was attributed to the synergistic effects of more visible light absorption and minimum electron hole recombination caused by the Fe ions incorporated into the crystal lattice of TiO₂. Density functional theory calculations further confirmed the role of Fe on the electronic structure of TiO₂.

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1. Introduction

Nitrogen oxides (NO_x), mainly produced from combustion of fossil fuels, are considered as a major contributors to atmospheric environmental problems, such as urban haze, photochemical smog, acid rain, and so on [1,2]. NO_x concentration in the atmosphere has greatly increased over the past few decades because of the increased number of coal burning, motor vehicles, and industrial emission [1]. The conventional approaches, such as selective catalytic reduction (SCR), wet scrubbing, adsorption, biofiltration, and catalytic decomposition can remove NO_x from emission sources; however, they are not economically feasible for the removal of NO at parts per billion (ppb) levels in urban environments [3,4]. Semiconductor photocatalysis, as a “green” technology, which utilize natural sunlight to purify air pollutants of low concentration at ambient conditions, has been used to remove NO_x [5–13].

Since the discovery of photocatalytic splitting of water on a titanium dioxide (TiO₂) electrode in 1972 [14], TiO₂ has long been a promising candidate for photocatalysis applications due to its strong photocatalytic oxidation performance, photostability,

natural abundance, and nontoxicity [15]. However, the relatively large band gap of TiO₂ (3.0–3.2 eV) limits its application in the visible light region (400 nm < λ < 750 nm), which accounts for 43% of incoming solar energy [3,16]. Therefore, developing visible light-responsive photocatalysts with high efficiency and stability are desirable and has become one of the most important topics in environmental photocatalysis [17,18]. Metal/nonmetal elements doping, narrower band gap semiconductor coupling, hydrogen treatment and photosensitization with dyes have been applied to enhance the visible light activity of TiO₂ [19–27].

Metal element doping is one of the typical approaches to extend the spectral response of TiO₂ to the visible-light region. Some metal elements, such as Fe, V, Co, Mo and Cr have been employed to tune the electronic structure and enhance the photocatalytic activity of TiO₂ [21,28–32]. Among these elements, Fe has attracted special attention as the ionic radius of Fe³⁺ (0.64 Å) is similar to that of Ti⁴⁺ (0.68 Å), resulting in easier insertion of Fe³⁺ into the crystal structure of TiO₂ [33]. As a dopant, however, the role of Fe³⁺ is still controversial. Some authors have suggested that the detrimental effect of Fe³⁺ as a promoter increases the rate of charge recombination, while other authors have reported on the beneficial effects of Fe³⁺ in the separation of photogenerated electrons and holes and in the shift of the absorption edge into the visible-light range with the narrowing of the band gap, thus increasing photocatalytic activity [31,34,35]. It is known that the role of Fe is determined by doping levels. The solubility limit of Fe in TiO₂ is

* Corresponding author. Tel.: +86 10 62849123; fax: +86 10 62849123.

E-mail address: honghe@rcees.ac.cn (H. He).

¹ Present address: Materials Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, United States.

1.0%, with separate α -Fe₂O₃ or Fe₂TiO₅ phases forming above this limit [36]. A separate Fe₂O₃ phase is detrimental to oxygen activation and photocatalytic activity [35]. Therefore, high Fe doping levels may decrease photocatalytic activity. On the other hand, surface or bulk doping may also influence the role of Fe. It is difficult for photogenerated holes or electrons trapped at bulk-doped Fe ions to migrate to the surface without recombination [37]. Experimental and theoretical computation results suggest that Fe ions on the surface may increase photocatalytic activity, while Fe ions in bulk may have a negative effect [37].

Although the state of Fe has great influence on photocatalytic activity, it has not been systematically investigated. We synthesized different Fe/TiO₂ catalysts and studied the influence of Fe on the structure and performance of Fe/TiO₂ as a photocatalyst to remove gaseous NO in air under visible light.

2. Experimental

2.1. Materials preparation

The Fe/TiO₂ catalysts were synthesized by facile co-precipitation method using Fe(NO₃)₃·9H₂O (≥98.5%) as a Fe precursor and Ti(SO₄)₂ (≥96%) as a Ti precursor (the molar content of Fe was 0.1%, 0.3%, 0.5%, 0.7% and 1%) and 25 wt% NH₃·H₂O as precipitator. After the pH of the mixed solution rose to 10 in the co-precipitation process, the precipitate cakes were first filtrated and washed by distilled water, and then desiccated at 100 °C for 12 h and calcined at 400 °C for 6 h under air conditions (the heating rate kept at 5 °C/min). The catalysts were signified by Fe $\%$ T (x means the molar content of Fe). Pristine Fe₂O₃ and TiO₂ were synthesized using Fe(NO₃)₃·9H₂O and Ti(SO₄)₂ as precursors, respectively.

Fe0.1%T catalyst was also prepared by the homogeneous precipitation method. The aqueous solutions of Fe(NO₃)₃·9H₂O (≥98.5%) as Fe precursors and Ti(SO₄)₂ (≥96%) as Ti precursors were mixed with required molar ratios. Excessive urea aqueous solution was then added into the mixed solution. The solution was heated to 90 °C and held there for 12 h under vigorous stir. After filtration and washing with deionized water, the resulting precipitant was dried at 100 °C overnight and subsequently calcined at 400 °C for 6 h in air condition (the heating rate kept at 5 °C/min). The catalyst was signified as Fe0.1%T-h. We also prepared Fe0.1%T catalyst using conventional wet impregnation method for comparison. The precursor was commercial anatase (Degussa). The catalyst was signified as Fe0.1%T-i.

2.2. Catalytic measurements

The photocatalytic experiments for the removal of NO were similar to our previous work [38], and are fully described in SI. Briefly, a 500 W commercial xenon arc lamp (Beijing TrusTech Science and Technology Co., China) was used as the light source. Two optical filters were used to obtain light in the 420–700 nm range, and the integrated light intensity was 35.8 mW/cm² (FZ-A, radiometer, Photoelectric Instrument Factor of Beijing Normal University). The weight of the photocatalyst used for each experiment was kept at 0.05 g. The initial concentration of NO was diluted to about 400 ppb by the air stream. The desired humidity level of the NO flow was controlled at 55% by passing the nitrogen streams through a humidification chamber. The total flow rate was controlled at 1.2 L min⁻¹. The concentration of NO, NO₂ and NO_x was continuously measured by a chemiluminescence NO_x analyzer (Thermo Environmental Instruments Inc., Model 42i), which monitors NO, NO₂, and NO_x (NO_x represents NO + NO₂) with a sampling rate of 0.7 L min⁻¹.

In the data analysis, the NO conversion, NO₂ selectivity, and NO_x conversion were defined as follows:

$$\text{NO conversion} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}$$

$$\text{NO}_2 \text{ selectivity} = \frac{[\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}$$

$$\text{NO}_x \text{ conversion} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}]_{\text{in}}}$$

Since NO₂ is more toxic than NO, the photocatalyst performance should be evaluated by the NO_x conversion, or the NO conversion in conjunction with the NO₂ selectivity.

2.3. Catalyst characterization

The actual ratio of Fe in Fe/TiO₂ products was detected using inductively coupled plasma optical emission spectrometer (ICP-OES).

The surface area of the catalyst was determined with a physisorption analyzer (Autosorb-1C-TCD, Quantachrome) by N₂ adsorption-desorption at 77 K. The surface area (S_{BET}) was determined by applying the Brunauer-Emmett-Teller (BET) method to the adsorption isotherm in the partial pressure range of 0.05–0.35.

The crystalline structure of the catalysts was determined by a powder X-ray diffractometer (XRD; X'Pert PRO, PANalytical, Netherlands) using Cu K α (λ = 0.15406 nm) radiation at 40 kV and 40 mA. The data of 2 θ from 20° to 80° were collected at 8°/min with the step size of 0.07°.

Raman spectra of the catalysts were recorded at room temperature on a UV resonance Raman spectrometer (UVR DLPC-DL-03), which consisted of three optional exciting lasers (244, 325, and 532 nm), a three-stage grating spectrograph, and a CCD detector cooled by liquid nitrogen. The instrument was calibrated against the Stokes Raman signal of Teflon at 1378 cm⁻¹. A 325-nm He-Cd laser was also used as an exciting source for the measurement of UV Raman. The spectra resolution was 2.0 cm⁻¹. All Raman spectra used in the paper were original and unsmoothed.

The UV-vis diffuse reflection spectra of the catalysts over the range of 200–800 nm were recorded at room temperature with a diffuse reflectance UV-vis spectrophotometer (U-3310, Hitachi), using BaSO₄ as reflectance standard.

The photoluminescence (PL) spectra were measured in a home-built laser induced luminescence spectrograph. The photoluminescence signal was collected with an ellipsoidal collecting mirror and focused onto a 320 mm monochromator (Jobin-Yvon Triax 320) by passing through a filter with cutoff wavelength below 360 nm. A charge-coupled device (Jobin-Yvon Spectrum One CCD 3000) was mounted at the focal plane in the exit of the monochromator to detect the luminescence signal. Prior to the experiments, the wavelength calibration of this setup was carried out with a mercury lamp. A 325-nm He-Cd laser was used as the exciting source for the measurement of photoluminescence spectra.

The X-band electron paramagnetic resonance (EPR) spectra were recorded at room temperature using a Bruker A300-10/12 EPR spectrometer.

The XANES of Fe K and Ti K edges were measured in a transmission mode at room temperature on BL-7C beam line, Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (IMSS-KEK), Japan. Fe foil, FeO, magnetite Fe₃O₄ and hematite Fe₂O₃ were used as reference samples. The storage ring was operated at 2.5 GeV with 300 mA as an average storage current. The synchrotron radiation beam line was monochromatized with a Si (1 1 1) double crystal monochromator,

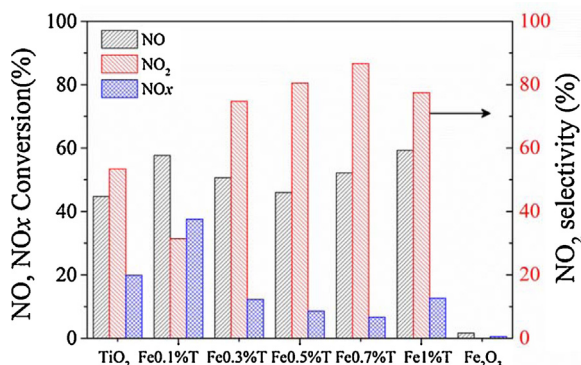


Fig. 1. NO conversion, NO_x conversion and NO₂ selectivity at 0.5 h over Fe_x%T ($x = 0.1, 0.3, 0.5, 0.7, 1$) catalysts and pure oxides including TiO₂ and Fe₂O₃.

and mirrors were used to eliminate higher harmonics. The incident and transmitted beam intensities were monitored using ionization chambers filled with pure N₂. XAFS data were analyzed using the REX2000 program (Rigaku Co.). XANES spectra were normalized with edge height and then taken the first-order derivatives to compare the variation of absorption edge energies.

2.4. DFT calculations

DFT calculations were performed using CASTEP package on the basis of the plane-wave-pseudo-potential approach. The Perdew–Burke–Ernzerhof (PBE) of the generalized gradient approximation (GGA) was used as the exchange–correlation function. The interaction between valence electrons and the ionic core was described by the ultrasoft pseudopotential. Calculations were carried out with a Monkhorst–Pack k -point mesh of $(2 \times 2 \times 1)$ and a plane-wave cutoff of 380 eV.

The initial geometry configurations were optimized by the Broyden, Fletcher, Goldfarb and Shannom (BFGS) minimizer for spin polarized systems with different initial numbers of spin-up and spin-down electrons. The spin occupation numbers were then optimized during the electronic iterations. The energetic convergence threshold for the self-consistent field (SCF) is 5.0×10^{-7} eV/atom. The convergence tolerance parameters of optimized calculations were a maximum energy of 1.0×10^{-5} eV/atom, a maximum force of 0.03 eV/Å, a maximum stress of 0.05 GPa and a maximum displacement of 1.0×10^{-3} Å.

The TiO₂ (1 0 1) surfaces were modeled by vacuum slabs. According to previous research [39], we have selected a slab of Ti₄₈O₉₆ with surface area of 11.09×11.41 Å² (see Fig. S1a), which contained eight O–Ti–O tri-layers (four periodic planes) and was separated by a vacuum gap of 20 Å thicknesses. Thus, the length in each direction

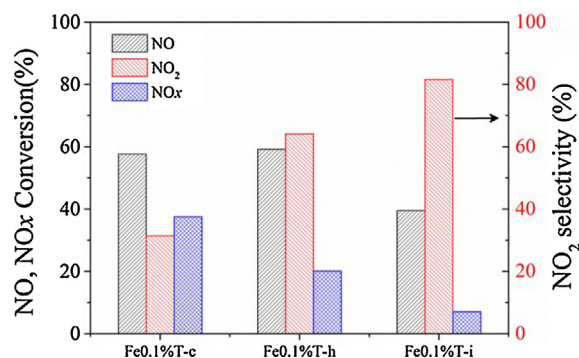


Fig. 2. NO conversion, NO_x conversion and NO₂ selectivity at 0.5 h over Fe_{0.1}%T-c, Fe_{0.1}%T-h and Fe_{0.1}%T-i.

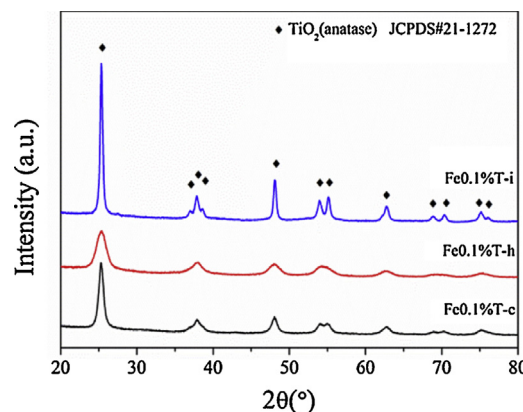


Fig. 3. XRD patterns of Fe_{0.1}%T prepared with different methods.

was long enough, so that self-interactions among the impurities could be ignored. The top six tri-layers were relaxed, while the bottom two tri-layers were fixed to mimic the bulk region. The surface sites, namely, the bridging two-fold coordinated oxygen atom (O_{2C}), three types of three-fold coordinated oxygen atom (O_{3C-1}, O_{3C-2}, and O_{3C-3}), and five/six-fold coordinated titanium atoms (Ti_{5C} and Ti_{6C}) are denoted in Fig. S1 as well. According to the experimental results, the model of Fe-doped surface (FeTi₄₇O₉₆) and Fe on the surface (FeTi₄₈O₉₆) was built by replacing a surface titanium atom with an iron atom and adding an iron atom at the interstice site on the surface of Ti₄₈O₉₆, respectively.

The DFT + U method can describe the electronic structure, band gaps and defect states of TiO₂ more correctly compare with the DFT method [40,41]. Therefore, after finishing the geometry optimizations, the DFT + U method was used to calculate the band structures and the projected density of states (PDOS) of the models. According to reference [42], the $U = 8.50$ eV of Ti 3d electrons and $U = 5.00$ eV of Fe 3d electrons were adopted in all energy calculation.

3. Results and discussion

The reaction of NO with air was negligible when the control experiments were performed with and without light in the absence of a photocatalyst (residence time 5.7 s). Basically, the removal of NO by photocatalysis can be described as follows: $\text{NO} \rightarrow \text{HNO}_2 \rightarrow \text{NO}_2 \rightarrow \text{HNO}_3$. NO₂ is the intermediate product of this reaction. When the site for the adsorption of HNO₃ is saturated or the concentration of hydroxyl radical is not satisfied to finish the last reaction, NO₂ would release into the air because of desorption. Fig. 1 shows the results of NO conversion, NO_x conversion, and NO₂ selectivity at 0.5 h for the photocatalytic removal of NO over Fe_x%T ($x = 0.1, 0.3, 0.5, 0.7, 1$) catalysts and pure oxides, including TiO₂ and Fe₂O₃. As we can see, pure Fe₂O₃ showed almost no activity. The conversion of NO was in the range of 45–60% over Fe_x%T ($x = 0.1, 0.3, 0.5, 0.7, 1$) and pure TiO₂, however, the selectivity of NO₂ (31%) was lowest over Fe_{0.1}%T, and therefore, the conversion of NO_x (38%) was highest over Fe_{0.1}%T. The activity of Fe_{0.1}%T was two times higher than that of pure TiO₂. Therefore, we selected Fe_{0.1}%T as the optimal content to carry out further investigations, such as the effects of synthesis methods on photocatalytic NO removal activities, and the relationship between catalyst structure and catalytic activity.

Fig. 2 shows the NO conversion, NO_x conversion and NO₂ selectivity results at 0.5 h for the photocatalytic removal of NO over Fe_{0.1}%T prepared with different methods. The Fe_{0.1}%T prepared with co-precipitation method (Fe_{0.1}%T-c) showed the highest NO_x conversion activity. Because the specific areas of the Fe_{0.1}%T prepared with different methods were very different (Table 1), we calculated specific activity normalized by surface area to exclude

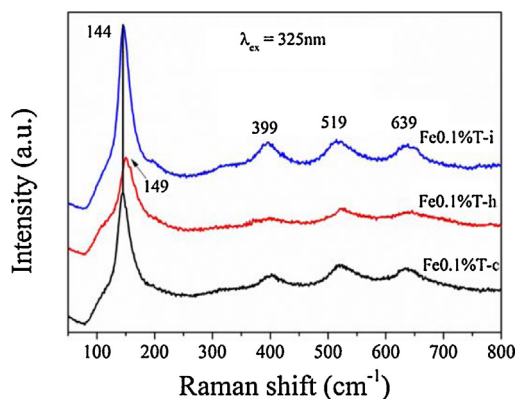


Fig. 4. UV Raman spectroscopy of Fe0.1%T prepared with different methods.

the effect of BET surface area on activity (Table 1). The specific activity of Fe0.1%T-c was three times higher than that of Fe0.1%T-h and Fe0.1%T-i.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to characterize the atomic composition of the catalysts. Table 1 shows the amount of Fe introduced into the structures as a molar percentage of Fe in relation to the molar percentage of Ti. The molar percentage of Fe was consistent with the initial amount of Fe added, that is 0.11%, 0.10% and 0.12% for Fe0.1%T-c, Fe0.1%T-h and Fe0.1%T-i, respectively.

The crystal structures of Fe0.1%T prepared with different methods were all anatase (JCPDS no.21-1272), as shown by the X-ray diffraction spectra in Fig. 3. No other crystalline phase (Fe_2O_3 or Fe_xTiO_y) was observed, which revealed that the Fe content in our samples was below the detection limits of the XRD instrument, or was very finely dispersed over the surface of the particles, or the Fe ions substituted the Ti atoms in the TiO_2 matrix due to the similar ionic radii of Fe^{3+} and Ti^{4+} [43].

Raman spectroscopy was used to clearly characterize the TiO_2 surface structure. The UV Raman spectra of Fe0.1%T prepared with different methods are shown in Fig. 4. Raman shifts at 144, 399, 519 and 639 cm^{-1} attributed to the Raman active modes of anatase with symmetries of E_g , B_{1g} , A_{1g} and E_g , respectively, were observed for all TiO_2 samples. These results indicate that the surface of Fe0.1%T prepared with different methods were in an anatase state. No Fe_2O_3 or other Fe related crystal phases were observed, in agreement with the XRD results.

The E_g feature of anatase (symmetric stretching vibration of O–Ti–O) at 144 cm^{-1} was studied in detail. The blue shift in the peak position for the catalyst prepared by homogeneous precipitation method (149 cm^{-1}) compared with the other catalyst (144 cm^{-1}) may be due to the formation of oxygen vacancies or size reduction (phonon quantum confinement model) in TiO_2 [44,45].

Fig. 5A and B shows the Fe K-edge X-ray absorption near-edge structures (XANES) of the reference samples, Fe0.1%T-c, Fe0.1%T-h, and Fe0.1%T-i catalysts and their corresponding first-order derivatives, respectively. The first-order derivative peak of the absorption coefficient appeared at 7120.5 eV for Fe^{2+} in FeO, while that for Fe^{3+} in pristine Fe_2O_3 appeared at 7127.1 eV . For the three catalysts, the XANES patterns of Fe K edge were different to those of any pristine oxides. This may be due to the low content of Fe and the formation of Fe–O bonds on the surface or the substitution of Ti in the lattice of TiO_2 . All three catalysts reached a maximum at 7127.1 eV in the first-order derivatives, indicating the presence of Fe^{3+} in these catalysts.

Fig. 5C and D shows the Ti K-edge XANES of TiO_2 -c, Fe0.1%T-c, TiO_2 -h, Fe0.1%T-h, TiO_2 (commercial anatase), Fe0.1%T-i and their corresponding first-order derivatives, respectively. Anatase TiO_2 was the main crystal phase in all samples and the oxidation state of

Table 1

Specific surface areas and specific activity of Fe0.1%T-c, Fe0.1%T-h and Fe0.1%T-i.

Catalysts	S_{BET} ($\text{m}^2\text{ g}^{-1}$)	Specific activity ($\%/\text{m}^2/\text{g}$)	Measured Fe (at%)
Fe0.1%T-c	105.4	0.356	0.11
Fe0.1%T-h	197.3	0.102	0.10
Fe0.1%T-i	68.3	0.103	0.12

Determined using Scherrer's equation (applicable from 3 to 200 nm).

Ti was +4. This was in good agreement with our previous XRD and Raman results. Therefore, from XANES analysis, we confirmed the presence of Fe^{3+} in our catalysts, which did not involve any change in the oxidation state of Ti.

Electron paramagnetic resonance (EPR) is a highly sensitive spectroscopic technique for examining paramagnetic species and can give valuable information about the lattice site in which a paramagnetic dopant ion is located. This highly sensitive technique can detect Fe ion levels down to 0.01% in metal oxide matrices [46]. The EPR spectra of Fe0.1%T prepared with different methods are shown in Fig. 6. Fe0.1%T-c and Fe0.1%T-h both showed intense signals at $g = 1.99$ and very weak signals at $g = 4.22$. According to previous reports [47,48], these two signals should be attributed to Fe^{3+} substituted for Ti^{4+} in the TiO_2 lattice ($g = 1.99$) and to Fe^{3+} substituted in the lattice adjacent to a charge-compensating oxide anion vacancy ($g = 4.22$), respectively. Analysis of the EPR results confirmed that Fe^{3+} ions were successfully incorporated into the crystal lattice of TiO_2 . The intensity of the EPR signal for Fe0.1%T-c was higher than that for Fe0.1%T-h, which indicated that more Fe^{3+} ions were successfully incorporated into the crystal lattice of TiO_2 prepared by co-precipitation method. The EPR spectra of Fe0.1%T-i showed almost no signals. This suggested that no Fe^{3+} ions were incorporated into the crystal lattice of TiO_2 prepared by conventional wet impregnation method. Therefore, Fe/ TiO_2 with different Fe states was obtained using different preparation methods.

The optical absorption properties of the Fe0.1%T catalysts were examined with UV–vis diffuse reflectance spectra (DRS) and the results are shown in Fig. 7. Fe0.1%T-i had weak absorption in the visible light region ($>400\text{ nm}$), whereas Fe0.1%T-c and Fe0.1%T-h exhibited red shifts of the absorption edge and a significant enhancement of light absorption at wavelengths of 400–600 nm. The band gap energies of Fe0.1%T-i, Fe0.1%T-h and Fe0.1%T-c were calculated to be 3.27, 3.13 and 2.93 eV, respectively. The narrowing of the band gap effectively improved the photocatalytic activity in the visible-light region. According to previous reports [47,49], the presence of metal ions in TiO_2 does not modify the position of the valence band edge of TiO_2 . Instead, it introduces new energy levels ($\text{Fe}^{2+}/\text{Fe}^{3+}$) of the transition metal ions into the band gap of TiO_2 . Therefore, the absorption edges shifts toward longer wavelengths for Fe/ TiO_2 should come from the electronic transition from the dopant energy level ($\text{Fe}^{2+}/\text{Fe}^{3+}$) to the conduction band of TiO_2 .

During the photocatalytic process, charge transfer and recombination are two competing reaction pathways. It is important to suppress the recombination rate and accelerate charge transfer to enhance photocatalytic activity. Photoluminescence (PL) emission spectra can be used to understand the fate of photo-generated electrons and holes in semiconductor particles since PL emission results from the recombination of free carriers [50,51].

The PL emission spectra of the catalysts are shown in Fig. 8, which reveal nearly identical peaks in shape and position for all catalysts. The PL intensity of Fe0.1%T-c was much lower than that of Fe0.1%T-h and Fe0.1%T-i, indicating that electron–hole recombination on the surface of Fe0.1%T-c was largely inhibited to generating more photoelectrons and holes to participate in the photocatalytic reaction. The reason is that Fe^{3+} incorporated into the TiO_2 lattice can act as an electron-trapped agent to promote electron-hole separation [52].

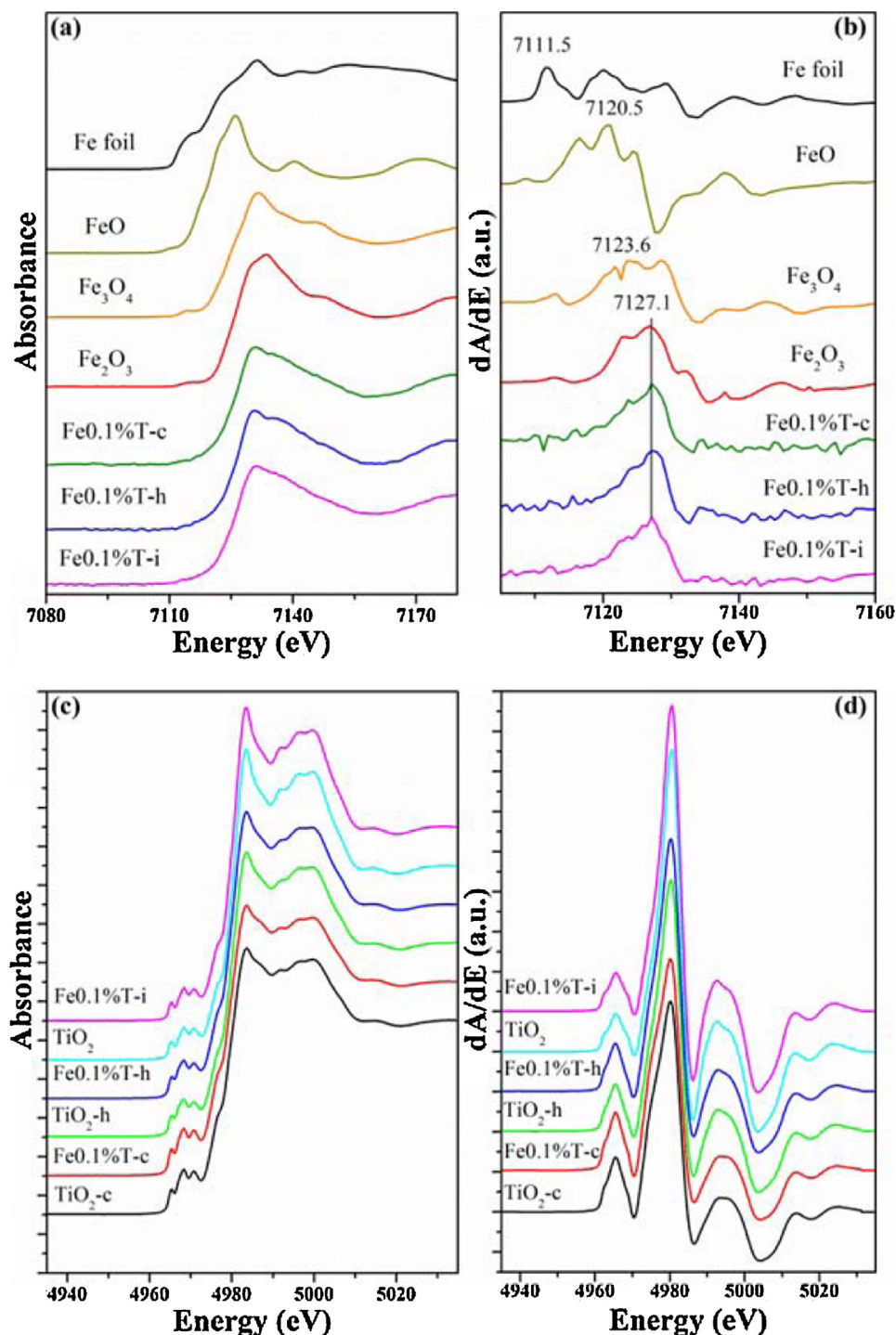


Fig. 5. (a) Fe K-edge XANES, (b) first-order derivatives of Fe K-edge XANES, (c) Ti K-edge XANES and (d) first-order derivatives of Ti K-edge XANES in different samples.

Based on the experimental characterization results, we performed theoretical calculations to gain a deeper understanding of the effect of Fe doping on the structural and electronic properties of the catalysts.

Anatase has a tetragonal crystal structure with space group $I4_1/AMD$ (1 4 1). The calculated lattice parameters of the pure TiO_2 model were $a=b=3.803 \text{ \AA}$ and $c=9.695 \text{ \AA}$ at ambient conditions, which were in good agreement with the previous experiment values of $a=b=3.782 \text{ \AA}$ and $c=9.502 \text{ \AA}$ [53]. When $U=8.5 \text{ eV}$ for the Ti 3d electrons was adopted in energy calculations, the calculated band gap of pure anatase TiO_2 was 3.26 eV , which was in

agreement with our experimental values and previous research [42]. Because (1 0 1) is the majority exposed facets of anatase, we optimized the structure of the perfect TiO_2 (1 0 1) surface (Fig. 9(a)). The most important outward relaxations were those of O_{3C-1} and Ti_{6C} atoms (0.19 and 0.23 \AA , respectively), while the Ti_{5C} atoms moved inward by -0.14 \AA . Therefore, the O_{3C-1} atoms were located above the Ti_{5C} atoms on the relaxed surface, as shown in Fig. S1. The surface configuration was consistent with previous reports [54–57], indicating that our calculation methods and results were reasonable and valid. Based on the results, we construct a Fe-doped surface model ($\text{FeTi}_{47}\text{O}_{96}$) and Fe on the surface model ($\text{FeTi}_{48}\text{O}_{96}$)

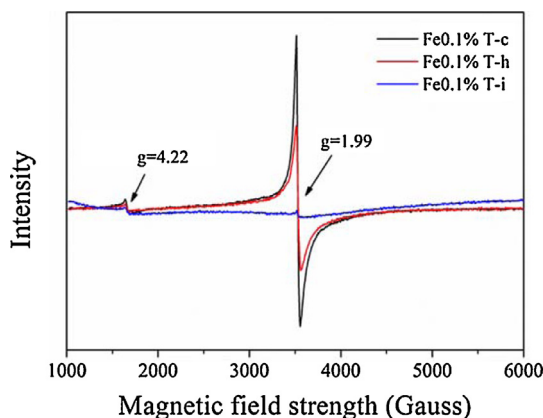


Fig. 6. ESR spectra of Fe0.1%Ti prepared with different methods.

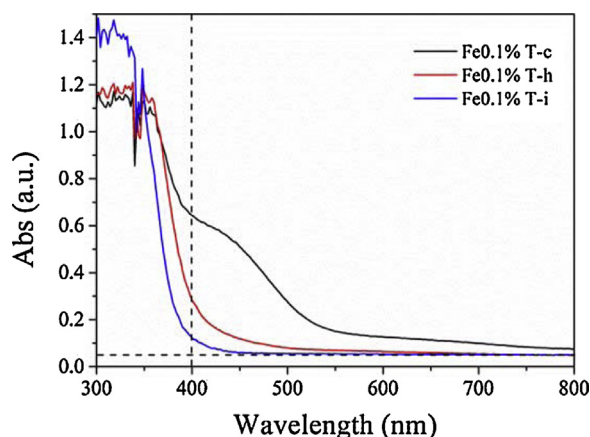


Fig. 7. UV-vis diffuse reflectance spectra of Fe0.1%Ti prepared with different methods.

representing the catalysts prepared by co-precipitation method and conventional wet impregnation method, respectively.

For the Fe-doped surface ($\text{FeTi}_{47}\text{O}_{96}$) model, there were two possible surface sites (Ti_{5C} and Ti_{6C}) for Fe atom substitution. Comparing the total energies of the two possible optimized configurations of the Fe-doped surface ($\text{FeTi}_{47}\text{O}_{96}$) model indicated that the Ti_{5C} site was energetically favored. Fig. 9(b) exhibits the relaxed configuration of a Fe atom substituting a Ti atom at the Ti_{5C} site. The substitution Fe atom was connected to neighboring O atoms and the optimized Fe–O bond lengths were 1.972, 1.898, 1.971, 1.907 and 1.758 Å. Compared with the original Ti–O bond lengths (1.986, 2.067, 1.987, 1.781 and 1.832 Å) of the $\text{Ti}_{48}\text{O}_{96}$ surface model (Fig. 9(a)), the substitution of Fe atom for Ti atom did not lead to significant lattice distortion. For the Fe on the surface ($\text{FeTi}_{48}\text{O}_{96}$), the energetically favored model is shown in Fig. 9(c). After optimization, the lengths of the Ti–O bonds nearest the Fe atom were 2.112, 1.887, 2.029, 2.026, 1.886, 2.115, 2.003 and 2.003 Å. Compared with

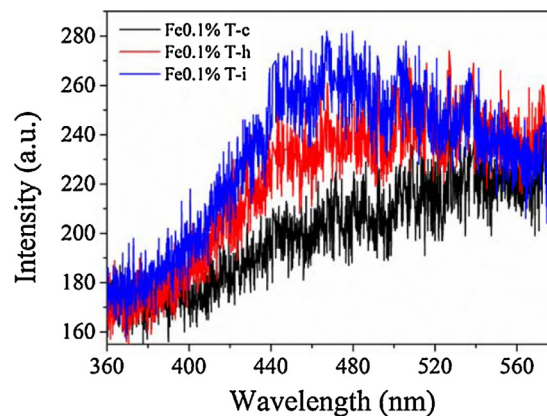


Fig. 8. Photoluminescence (PL) emission spectra of the catalysts.

the original Ti–O bond lengths (1.8662, 1.832, 1.987, 1.986, 1.832, 1.862, 1.943 and 1.942 Å) of the $\text{Ti}_{48}\text{O}_{96}$ surface model (Fig. 9(a)), the Fe atom added on the surface of the $\text{Ti}_{48}\text{O}_{96}$ model did not lead to significant lattice distortion.

The band structures of the $\text{Ti}_{48}\text{O}_{96}$, $\text{FeTi}_{47}\text{O}_{96}$ and $\text{FeTi}_{48}\text{O}_{96}$ surface models were obtained by the DFT + U calculations, as shown in Fig. S2. The calculated band gaps were 2.59, 1.61 and 2.53 eV for the $\text{Ti}_{48}\text{O}_{96}$, $\text{FeTi}_{47}\text{O}_{96}$ and $\text{FeTi}_{48}\text{O}_{96}$ surface models, respectively. This indicated that the substitution of Fe atom for Ti atoms lead to a narrowing of the band gap, which was consistent with the experimental results (Fig. 7).

To understand the origin of the band gap variation, total density of states (DOS) and projected density of states (PDOS) were calculated and plotted in Fig. 10, with up-spin DOS above zero and down-spin DOS below zero. For the pure surface $\text{Ti}_{48}\text{O}_{96}$ model (Fig. 10(a)), the valence band (VB) consisted of Ti 3d and O 2p states, and the conductive band (CB) primarily consisted of Ti 3d states, which was consistent with previous studies [39,42]. For the $\text{FeTi}_{47}\text{O}_{96}$ model, the Fe 3d states were located at the bottom of the CB and partially overlapped with the energy band of TiO_2 , as shallow donor energy levels. According to Fig. 10(b), Fe doping also induced an acceptor state at the top of the VB as shallow acceptor energy levels, which was caused by hybridization between the Fe 3d, O 2p and Ti 3d states. Therefore, these impurity states prolonged the lifetimes of photoexcited carriers and enhanced photocatalytic performance. For the $\text{FeTi}_{48}\text{O}_{96}$ model, the Fe 3d states were located at the bottom of the VB and overlapped with the VB of TiO_2 . Two spin-parallel electronic levels were located at 1.08 and 1.54 eV from the top of the VB, as shown in Fig. 10(c). The location of the two levels suggested a deep donor level and accelerated recombination of photoexcited electron and holes. The calculated results indicated that the electronic structure of TiO_2 was changed by the Fe atom.

Experimental characterization demonstrated that Fe ions incorporated into the crystal lattice of TiO_2 narrow the band gap of the catalysts, enhance the visible light absorption and improve the separation efficiency of electron hole pairs. Theoretical calculations

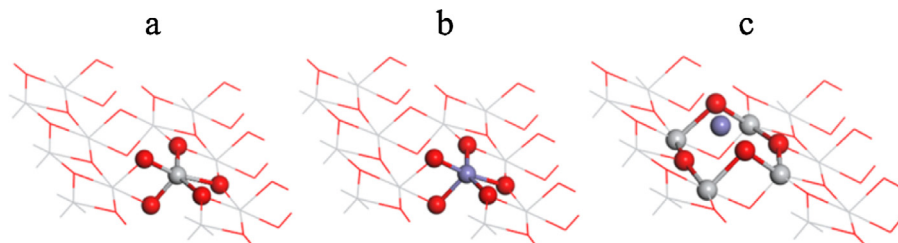


Fig. 9. Relaxed structure of the first layer of (a) $\text{Ti}_{48}\text{O}_{96}$, (b) $\text{FeTi}_{47}\text{O}_{96}$ and (c) $\text{FeTi}_{48}\text{O}_{96}$.

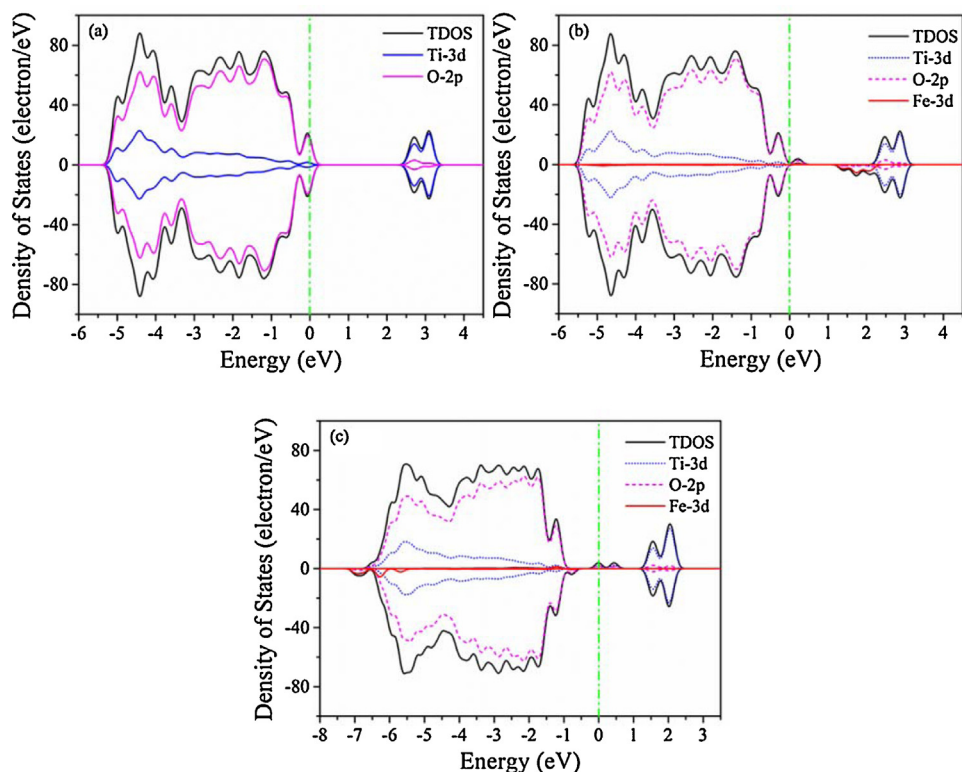


Fig. 10. The DFT+U density of states for (a) $\text{Ti}_{48}\text{O}_{96}$, (b) $\text{FeTi}_{47}\text{O}_{96}$ and (c) $\text{FeTi}_{48}\text{O}_{96}$. The energy zero is taken as the Fermi level and displayed with a green dashed line.

showed that the model of Fe incorporated into the crystal lattice of TiO_2 had the narrower band gap and shallow acceptor levels to promote the separation of electron and hole in the band gap. The theoretical calculation results verified the experimental characterization results, and indicated that the importance of Fe replaces the Ti in the TiO_2 lattice for the enhancement of the photocatalytic activity.

4. Conclusions

The present study demonstrated the importance of Fe ions incorporated into the crystal lattice of TiO_2 . The incorporated Fe ions substituted the octahedrally coordinated Ti^{4+} ions in the TiO_2 lattice, which extended the visible light absorption; and hence, promoted the formation of electron–hole pairs. Furthermore, the doping of Fe increased the electron–hole separation efficiency because Fe^{3+} incorporated into TiO_2 can act as an electron-trapped agent. Fe ions substituted the Ti ions of TiO_2 prepared by the co-precipitation method, however, no Fe ions were incorporated into the crystal lattice of the TiO_2 prepared by the conventional wet impregnation method. The structural differences caused by different preparation method determined the photocatalytic activity of Fe/TiO_2 .

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.05.003>.

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